



MUTU11.001CP1

PATENT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant	:	Lee, et al.
Appl. No.	:	10/666,618
Filed	:	September 18, 2003
For	:	SUPPORTED METALLOCENE CATALYST AND OLEFIN POLYMERIZATION USING THE SAME
Examiner	:	Pasterczyk, J. W.
Group Art Unit	:	1755

**DECLARATION OF BUN YEOUL LEE**

United States Patent and Trademark Office  
P.O. Box 2327  
Arlington, VA 22202

Dear Sir:

I, Dr. Bun Yeoul Lee, declare as follows:

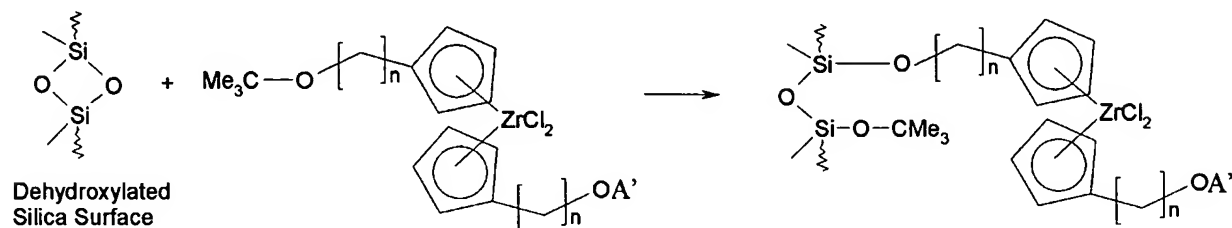
1. I am one of the inventors of the subject application. I have a Ph.D. of Seoul National University in the department of chemistry and many years of experience working in research and development on olefin polymerization catalysts. I am currently an assistant manager in Technology Center of LG Chemical Ltd.

2. I am familiar with the prosecution of the present application, including the Office Action mailed October 15, 2004, the references cited therein, and the Amendment accompanying this Declaration.

3. I am advised that pending Claims 4-10 and 15-20 have been rejected as obvious over as obvious over any of Korean Laid-Open Patent 98-25282 (hereinafter "Lee II"), US 5,814,574 (hereinafter "McNally"), EPO 0 839 836 (hereinafter "Sancho Royo"), and U.S. Publ. No. 2003/0144135 A1 (hereinafter "Llinas et al.").

4. I and my co-inventors have developed olefin polymerization catalysts that exhibit unexpectedly superior activity when compared to conventional olefin polymerization catalysts.

Unlike conventional catalysts, the catalysts of the present invention use a specific, functionalized metallocene compound reacted with a dehydroxylated silica support material to produce a supported metallocene catalyst:



The metallocene catalyst includes a moiety of formula A'-O, wherein A' is a carbon-based group such as tert-butyl or tetrahydropyranyl, that reacts with a reactive siloxane (Si-O-Si) group of the support material to produce a supported metallocene catalysts exhibiting unexpectedly superior activity and which are prepared by a method that does not result in formation of undesirable reaction by-products such as alcohol. The supported catalysts exhibit reduced reactor fouling, superior activity, and yield a better defined bulk density of polymer when compared to metallocenes containing other alkoxy groups, as discussed in the Examples of the present application.

5. Table 1 provides experimental data including measurements of catalyst activity (as kg of polyethylene produced per mmol of zirconium in the catalyst) of five different catalysts according to our invention. As the data demonstrate, the type of functional group included in the metallocene compound can have a significant effect on activity of the supported catalyst prepared from it. When a functional group (X) is a tert-butyl consisting of only carbon and hydrogen without a heteroatom such as oxygen, its supported catalyst (Example 5) is especially active for ethylene polymerization. We have also discovered that functional groups of the formula -C-OX can be incorporated into the metallocene compound to yield supported catalysts that also exhibit particularly good activity. Such catalysts include those incorporating a moiety of Chemical Formula 1 as depicted in the present application, wherein the Z atom is bonded to a silicon atom of a siloxane group (Si-O-Si) in the dehydroxylated silica support and the radical portion (X = -CR'<sub>2</sub>G) is bonded to an oxygen atom of the siloxane group. Our supported catalysts where X (-CR'<sub>2</sub>G) include only carbon and hydrogen atoms, for example, a hydrogen, an alkyl, cycloalkyl,

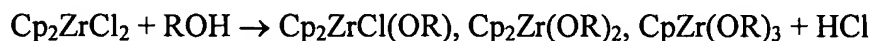
aryl, alkenyl, alkylaryl, arylalkyl, or arylalkenyl radical having up to 20 carbon atoms, or a phenyl or substituted phenyl, are especially active for olefin polymerization.

Table 1.

	Functional Group (A')	Zr (mmol)	Al/Zr ratio	Activity (kg PE / mmol Zr)
Example 1	[MeOCH <sub>2</sub> O(CH <sub>2</sub> ) <sub>6</sub> Cp] <sub>2</sub> ZrCl <sub>2</sub>	0.0156	64	3.40
Example 2	[MeC(Me)(OMe)O(CH <sub>2</sub> ) <sub>6</sub> Cp] <sub>2</sub> ZrCl <sub>2</sub>	0.0143	70	4.90
Example 3	[(C <sub>5</sub> H <sub>9</sub> O)O(CH <sub>2</sub> ) <sub>6</sub> ] <sub>2</sub> ZrCl <sub>2</sub>	0.0137	73	5.84
Example 4	[MeCH(OEt)O(CH <sub>2</sub> ) <sub>6</sub> Cp] <sub>2</sub> ZrCl <sub>2</sub>	0.0143	70	5.52
Example 5	[Me <sub>3</sub> CO(CH <sub>2</sub> ) <sub>6</sub> Cp] <sub>2</sub> ZrCl <sub>2</sub>	0.0150	67	6.73

(Polymerization conditions: temp. 80 °C, MAO (Al) 1.0 mmol, C<sub>2</sub> pressure 9 bar)

6. In contrast to the catalysts of the present invention, conventional catalysts such as those disclosed in EPO 0 839 836 incorporate a functional group of formula -C-SiR<sub>2</sub>X (X = alkoxy) in which the silicon atom is bonded to an oxygen atom of a silanol group in the silica support surface and the radical portion (X = alkoxy) reacts with a hydrogen of the silanol group of a hydroxylated silica support to yield a free alkyl alcohol (XH). Polymerization activity results for examples of such supported metallocene systems are provided in Table 2. Side reactions can occur during preparation of such catalysts, however, such as the following reaction:



Such side reactions can result in leaching when activated with methylalumoxane. Accordingly, while an R'O-Si group on the metallocene compound can react with an Si-OH group of the hydroxylated silica support to produce a strongly-bound, supported metallocene catalyst via Si-O-Si bond formation, alkyl alcohol (R'O-H) is also formed as by-product during the reaction, which can act as a catalyst poison to lower activity of the final catalyst, and can result in substantial catalyst fouling. Such by-products are not produced in the reaction used to prepare the catalysts of our invention.

Table 2.

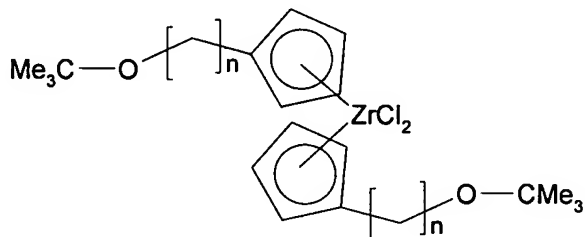
	Metal (mmol)	Al/Metal ratio	Activity (kg PE / mmol Metal)
Comparative Example 1	Zr, 0.02	11	3.03

Comparative Example 2	Zr, 0.01	22	4.2
Comparative Example 3	Ti, 0.02	11	1.4
Comparative Example 4	Hf, 0.02	11	0.6

(Polymerization conditions: temp. 70 °C, MAO (Al) 0.22 mmol, C2 pressure 7 bar)

7. Catalysts have been prepared according to the teachings of Lee II, McNally, Sancho Royo, and Llinas et al. A catalyst prepared according to the method of Lee II exhibited an activity of 1.51 kg PE / mmol Zr hr. A catalyst prepared according to the method of McNally exhibited an activity of 0.40 kg PE / mmol Zr hr. A catalyst prepared according to the method of Sancho Royo exhibited an activity of 3.05 kg PE / mmol Zr hr. A catalyst prepared according to the method of Llinas et al. exhibited an activity of 3.24 kg PE / mmol Zr hr). These activities are substantially less than those of the most active catalysts of our invention.

8. We have also discovered that the length of the carbon chain between the Cp ring and the active functional group can affect catalyst activity. Table 3 provides activities of supported catalysts produced by reaction of a functionalized metallocene compound of formula:



wherein A' is tert-butyl, and a dehydroxylated silica (dried at 800°C). As demonstrated by the data, a carbon chain length (n) of 4 to 8 unexpectedly results in a supported catalyst that is especially active for ethylene polymerization, in contrast to the only trace activity of a catalyst where the carbon chain length (n) is 2.

Table 3.

Example <sup>1</sup>	Carbon Length (n)	Yield (g)	Activity <sup>2</sup>	Mw	Mw/Mn
1	C2	Trace	-	-	-
2	C4	2.50	100	133,780	2.60
3	C6	5.80	232	147,390	2.61
4	C8	2.74	110	92,830	3.02

<sup>1</sup> condition: 500 mL Endrew glass,  $T_p=80^\circ\text{C}$ ;  $t=30$  min;  $p(\text{C}_2\text{H}_4)=4.0$  bar, cat.=50 mg, mole ratio Al/Zr=500

Appl. No. : 10/666,618  
Filed : September 18, 2003

$^2$  g PE / g Cat · hr

9. I declare that all statements made herein are true, and that all statements made upon information and belief are believed to be true, and further, that these statements were made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that willful, false statements may jeopardize the validity of the application, or any patent issuing thereon.

Dated: \_\_\_\_\_

By: Lee Bun Yeoul

S:\DOCS\RMTRMT-6410.DOC  
021105